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Efficient use of Ethylene Oxide in Vinyl Sulphone Industry

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Abstract

Vinyl sulphone production includes mainly 4 unit processes which are Chlorosulphonation, Reduction, Condensation, and Esterification. Vinyl sulphone is the highest export dye intermediate. Vinyl sulphone industry in India received a set back in the late nineties due to world competition and insistence on environmental regulations by the controlling authorities. Excess of ethylene oxide is used in condensation, Which is hazardous and it is used in excess as large quantity of Ethylene oxide is reacted with water as a side reaction forming glycols, and also ethylene oxide is soluble in water. So ethylene oxide is wasted in water and increases the volume of reactor.
This paper describes to minimize the quantity of water which is causing excess use of ethylene oxide in condensation reaction. Before condensation reaction there are two unit processes Chlorosulphonation and reduction from which we try to limit the quantity of water, so that water coming to condensation reaction is minimized to reduce the side reaction of ethylene oxide and water.

Key words – Vacuum pump, Ethylene oxide, Acetyl sulphonic Chloride, Sodium salt of acetyl sulphonil acid,Ethylene glycol

I. Introduction

Dyes and dye intermediates industry (represents the highest development of chemical technology) and forms an important link in the chain of other essential chemical industries. On one hand petrochemical industry and inorganic chemical industry act as upstream raw material supplier industries, and on the other, textile, leather, plastic, paint, fine chemicals and pharmaceutical industries act as the downstream consumer industries. The technology employed in dyes and dye intermediates industry covers almost all unit processes and unit operations of chemical synthesis. Indian Dyes and Dye Intermediates industry has exhibited substantial growth, particularly in the last 15 years. In this span of 15 years, the production tonnage has increased 3 times, whereas the export value in Rupees has increased 79 times. At present, export of dyes and dye intermediates is 50% of the total export of chemicals from India. The dyes and dye intermediates are being exported to developed countries also from India.

In condensation reaction excess of ethylene oxide is required. The amount of ethylene oxide is 1300kg per batch. In condensation reaction as per the stoichiometry 749.79 kg of ethylene oxide is required. So 550.20 kg of extra ethylene oxide is used in the condensation reaction. This extra ethylene oxide is wasted in the side reaction of ethylene oxide and water which forms ethylene glycols.
Also ethylene oxide is soluble in water. So ethylene oxide is wasted in water.

The current paper presents experiment for the removal of moisture(water) before reduction reaction by applying vacuum. This removes acidic water in filtration step so in the next step which is reduction, quantity of caustic lye is also minimized which also contains 52% of water. Also quantity of water used in reduction is too mush which also can be minimized.

II. Ethylene Oxide

Ethylene oxide was fiist prepared in 1859 by Wurtz from 2-chloroethanol (ethylene chlorohydrin) and aqueous potassium hydroxide . He later attempted to produce ethylene oxide by direct oxidation but did not succeed . Many other researchers were also unsuccessful . In 1931, Lefort achieved direct oxidation of ethylene to ethylene oxide using a silver catalyst. Although early manufacture of ethylene oxide was accomplished by the chlorohydrin process, the direct oxidation process has been used almost exclusively since 1940. Today about 9.6 x 106 t of ethylene oxide are produced each year worldwide. Ethylene Oxide (EO), sometimes referred to as oxirane, is the simplest cyclic ether. It is a colorless gas or liquid and has a sweet, etheric odor.

III. Ethylene Oxide Reaction With Water

Wurtz was the first to obtain ethylene glycol by heating ethylene oxide and water in a sealed tube . Later, it was noted that by-products, namely diethylene and triethylene glycol, were

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also founed in this reaction. This was the first synthesis of polymeric compounds of well-defined structure. Hydration is slow at ambient temperatures and neutral conditions, but is much faster with either acid or base catalysis . The type of anion in the catalyzing acid is relatively unimportant .

The rates of reaction of ethylene Oxide with water, and ethylene oxide with ethylene glycols to produce higher molecular weight ethylene glycols by addition polymerization are significantly faster than in neutral medium.However the rates are slower than in acidic medium.This can be seen in the figure which shows MEG selectivity versus pH values.

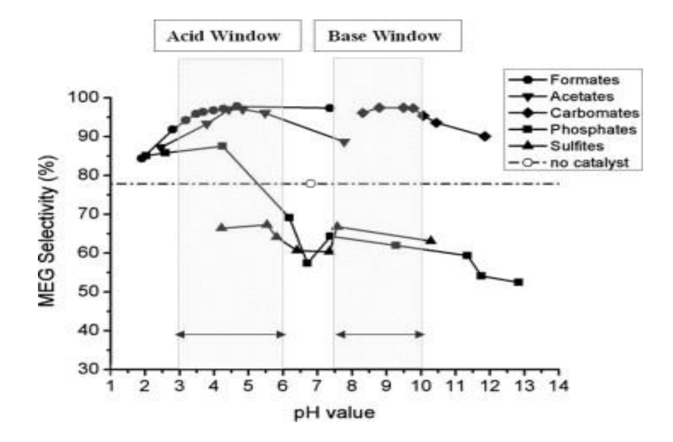


Figure 1. MEG selectivity with different PH.

A. Ethylene Oxide And Water Or Ethylene Glycol Reactions (Acidic Medium)

The rates of reaction of ethylene Oxide with water, and ethylene oxide with ethylene glycols to produce higher molecular weight ethylene glycols by addition polymerization increase as the pH decreases, and are significantly faster in an acidic medium (pH 1-2) than in a neutral medium.

B. Ethylene Oxide and Water or Ethylene Glycol Reactions (Basic Medium)

The rates of reaction of ethylene Oxide with water, and ethylene oxide with ethylene glycols to produce higher molecular weight ethylene glycols by addition polymerization are significantly faster than in neutral medium.However the rates are slower than in acidic medium.This can be seen in the figure which shows MEG selectivity versus PH values.

Table 1 Rate Constant For Different Medium

Temperature,	Acidic, *ka*,	Neutral,*C	Basic
20	0.32	0.22	0.34
30	1.00	0.55	1.0
40	2.5	1.9	3.06
60		11.9	17.0
80		60.6	77

IV. Experimental Procedure

A.Filtration in lab scale

Appratus needed for the experiment
Vacuum pump, Buchner funnel, Receiver Flask, Vacuum cork, Vacuum Flask

- Collect the sample of Acetyl sulphonyl Chloride and place the cake in the funnel.
- Start the vacuum pump from 130mmHg initially.
- Vacuum will increase with the removal of moisture which increases upto 450 mmHg.
- Measure the volume of water removed in the receiver flask, which is acidic.
- Weight the ASC cake and calculate amount of pure ASC.



Fig 1 Experimental set up of Vacuum Filtration

B. Reduction in lab scale



Fig 2 Reduction set up **Fig 3 Nitrite value set up**

The experimental set up of Reduction reaction is shown in Fig 2 and the procedure is as follow.
Reduction set up consist of Flask, Caustic lye thermopocket, pH indicator.

- Take 293 ml of Tap water in the beaker for getting proper dilution.
- Then take 100 grams of sodium bisulphate in the Beaker.
- Start stirring the mixture of water and sodium bisulphate.
- Add the cake of ASC which is obtained after the Vacuum filtration
- As the reaction of Acetyl sulphonyl chloride and sodium bisulphate and caustic lye is Exothermic, temperature increases.
- So to maintain the temperature at 40° C ice is added in the jacket.
- Two parameters should be controlled during the reaction which are temperature and pH.
- To get the Product Quantity we have to check the nitrite value and we get the quantity of product which is sodium salt of sulphinic acid(SSASA).

C. Condensation in lab scale

In condensation reaction charge 1180 ml of reduction mass and heat upto 55*C and control the pH at 7.5 by using 55% H_2SO_4 and start purging 64gm Ethylene oxide. Then check the completion of reaction by filter loss found in mother liquor, then cool the mass to 45*C and dry at 120*C

V. Results

A. Results of Vacuum Filtration Experiment

Mass of the cake	530gms
Moisture in the original ASC cake	60%
% moisture removed	39.42%
Caustic saved	53.20gms
Pure ASC	212gms
Water saved	27.66gms
Water saved in kg	519.40

B. Results of reduction reaction

SSASA	207.72gms
Conversion	97.9%
Water saved	149.23ml
Water saved in kg	2802.28kg
Nitrite value	17.5

Total amount of water saved from vacuum filtration and reduction experiment 519.40+2802.28=3321.68

C. Results of condensation reaction

Vinyl sulphone condensate	227.49 gms
Ethylene oxide added	64gms
Ehtylene oxide used	41.19gms
Ethylene oxide saved	22.89gms
Percentage EO unreacted From experiment	35.76%
Percentage EO unreacted in plant	42.30%
Ethylene oxide unreacted in Kg	464kg
Ethylene oxide which did not react with water	86kg

VI. Conclusion

Ethylene oxide is very hazardous and explosive compound to handle. By Adopting proper unit operation techniques by applying vacuum in the filtration step more moisture is removed, which removes acidic water and reduce the quantity of caustic lye in the next reaction i.e reduction. Caustic lye also contains 52% of water so water from this will be minimized and in reduction reaction the quantity of water is reduced considerably ,the total amount of water removed from both these steps is 3321.68 litres. So these quantity of water will not react with ethylene oxide in the condensation step. So quantity of ethylene oxide which forms glycols will be minimized also the ethylene oxide is soluble in water, so less ethylene oxide will be wasted in condensation reaction. Also cost of 1 kg of ethylene oxide is 90Rs,by performing this experiment we are able to save 86kg of ethylene oxide per batch without the addition of any unit process.So thus minimising the quantity of Ethylene oxide will decrease raw material cost, it will decrease glycol formation which increases COD , also it will decrease the volume of the reactor.

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